

Electrochemical reduction of dioxygen on a thioglycolic acid-capped CdTe quantum dots modified glassy carbon electrode

Mehdi Asgari · Maryam Shanehsaz ·
Mojtaba Shamsipur · Mahsa Behzad ·
Mohammad Ghannadi Maragheh

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Abstract A novel modified electrode was constructed by immobilizing thioglycolic acid-capped CdTe quantum dots (QDs) on a glassy carbon electrode (GCE) using Nafion ionomers. The results obtained by electrochemical impedance spectroscopy, cyclic voltammetry, and rotating disk electrode using the modified QDs–Nafion/GCE in a 0.20 M phosphate buffer of pH 7.0 revealed that the QDs act as effective mediators for the electrocatalytic reduction of dioxygen.

Keywords Quantum dot · CdTe · Modified electrode · Oxygen reduction reaction

1 Introduction

Because of critical importance of the oxygen reduction reaction (ORR) in life processes and in energy conversion systems such as fuel cells [1–3], much interest has been focused on the development of new materials for the catalytic electroreduction of dioxygen [1]. Thus, a variety of compounds including metal complexes with macrocyclic ligands [4], chelating agents [5, 6], porphyrins and phthalocyanines [7, 8], azobenzenes [9], and anthraquinones [10, 11] have been proposed as electrocatalysts for

modifying the electrode surfaces for dioxygen reduction. In recent years, a widespread use of carbon nanotubes [12, 13] and metal nanoparticles [14, 15] modified electrodes in electrocatalytic reduction of dioxygen has also been reported.

Quantum dots (QDs) are nanometer scale semiconductor crystals, composed of groups II–VI or III–V elements, possess exceptional photophysical properties which enable their application in many existing and emerging technologies [16]. Recently, many biological applications of QDs have been reviewed [17]. Meanwhile, QDs-based electrochemical bioassay has also become a favorite topic, due to their inherent miniaturization, high sensitivity, low cost, low power requirements, and ability to promote the direct electron transfer among the biomolecules and electrode surfaces [18, 19].

In continuation of our previous works on the electrocatalytic reduction of dioxygen on GCEs modified with different metal ion complexes [5, 6, 8] and some anthraquinones [10]. In this work, we report the first use of a novel modified electrode constructed by immobilizing thioglycolic acid-capped CdTe QDs at a GCE with Nafion ionomer for the electrocatalysis of ORR at neutral pH.

2 Experimental

All reagents were of analytical grade from Sigma or Merck companies, and used as received. All solutions were prepared with doubly distilled water. The supporting electrolytes used were 0.20 M phosphate- and acetate buffer solutions. CdTe QDs in a thiol-capped form were synthesized as reported by Zhang et al. [20] with some modifications. In brief, tellurium powder was chosen for preparation of NaH₂Te aqueous solution. Te powder was reduced using excessive sodium

M. Asgari (✉) · M. Behzad · M. G. Maragheh
NFCRI, NSTRI, Tehran, Iran
e-mail: mehdiasegari2002@yahoo.com

M. Shanehsaz
Department of Chemistry, Tarbiat Modares University, Tehran, Iran

M. Shamsipur
Department of Chemistry, Razi University, Kermanshah, Iran

borohydride in water under stirring and N_2 purging. After 8 h, the color of solution was changed from violet to white, and sodium tetra borate was precipitated. The fresh NaHTe thus prepared was added to a $CdCl_2$ solution containing thioglycolic acid under N_2 atmosphere. The molar ratio of Cd^{2+} :Te:TGA was set as 1.0:0.5:2.4. The pH of solution was adjusted to 11, and the mixture was then heated and refluxed at 100 °C for 4 h. The obtained QDs were precipitated with ethanol and then separated using centrifugation. Then, 1.0 g of the resultant precipitate was re-dispersed in 10 mL doubly distilled water and kept at 4 °C in dark.

For the preparation of QDs–Nafion/GCE, the surface of GCE was first mechanically polished with 0.05 μm α -alumina powder and rinsed thoroughly with acetone and doubly distilled water. The 4.9 mL of the synthesized QDs re-dispersed in doubly distilled water was added into 0.1 mL of 5 % Nafion suspension (the solvent is water) and, upon ultrasonication agitation for 5 min, a homogeneous stable QDs–Nafion suspension was obtained. The GCE was finally coated by casting of 20 μL of QDs–Nafion suspension and dried in oven at 35 °C.

All electrochemical experiments were carried out using an Ivium Compact-state Electrochemical Analyzer equipped with a personal computer for data storage and processing. Cyclic voltammetric experiments were performed in a conventional three-electrode cell [5, 6, 8, 10]. The temperature was maintained at 25.0 ± 0.5 °C, using a water thermostatic bath.

3 Results and discussion

The morphology of the prepared TGA-capped CdTe was studied by TEM (Fig. 1a). As seen, the QDs possess a spherical morphology and are homogeneously size distributed. The distribution histogram illustrated in Fig. 1 revealed an average particle size of about 3 nm. The QDs dispersed in a phosphate buffer of pH 7.4 showed a high stability within 3 months. The QDs stability was checked following their fluorescent stability.

The electrochemical impedance spectroscopy (EIS) was used to obtain information about the changes in charge transfer at the electrode surface during the modification process [21]. Figure 2 shows the Nyquist plots of Nafion/GCE (A), GCE (B) and QDs–Nafion/GCE (C) electrodes in the presence of 10 mM of $Fe(CN)_6^{3-/4-}$ in a buffer solution of pH 7.0. Obviously, the diameter of Nyquist circle on GCE (B) is very small, showing a facile charge transfer at the electrode. After Nafion casting on the electrode surface (A), a substantial increase in the diameter of the semicircle is observed, because Nafion acts as a mass transfer blocking layer which hinders the diffusion of ferricyanide toward electrode surface [22]. However, when QDs were

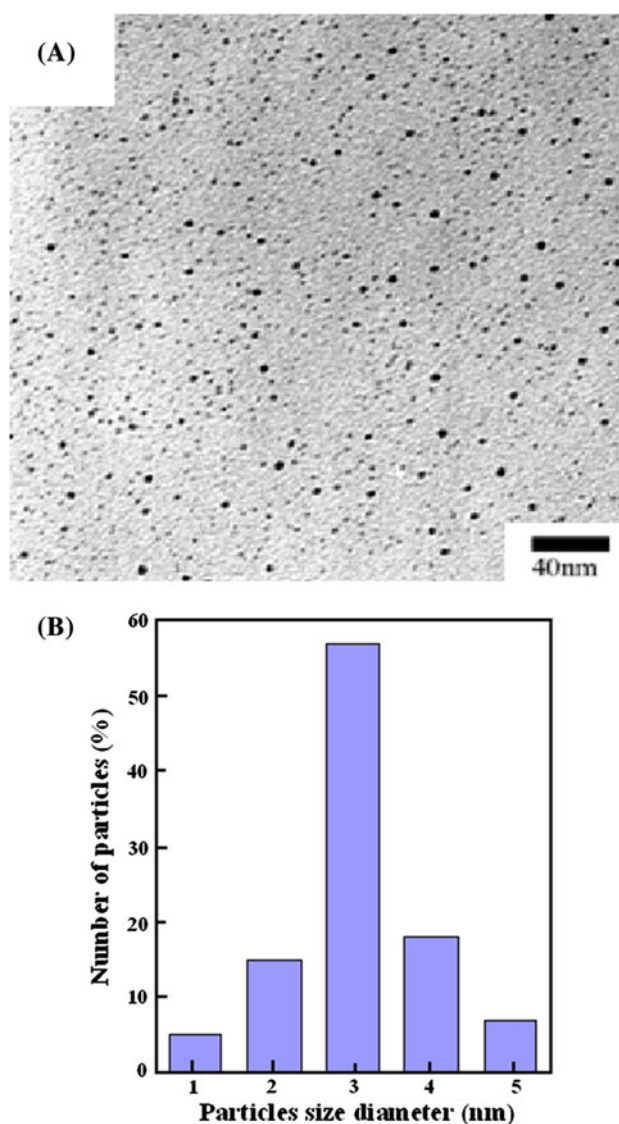


Fig. 1 TEM image (a) and size distribution diagram (b) of CdTe quantum dots

added into the Nafion film (C), the diameter of Nyquist circle decreased dramatically, showing that the QDs act as suitable electron-transfer interface between the EIS probe and the electrode surface.

In Fig. 3, curves c and d show the cyclic voltammograms of QDs–Nafion/GCE in a buffer solution of pH 7.0 in the absence and presence of O_2 , respectively, while a and b are the voltammograms of the bare GCE in the same buffer solution in the absence and presence of O_2 , respectively. The O_2 reduction at bare GCE (b) appears at -680 mV [vs. Ag/AgCl (3 M KCl)] and makes a small cathodic peak, while the O_2 reduction on the QDs–Nafion/GCE modified electrode gives a large peak at -460 mV (d). The cathodic peak current is increased due to the presence of saturated O_2 . Therefore, a decrease of 220 mV in overpotential and a large enhancement in peak current

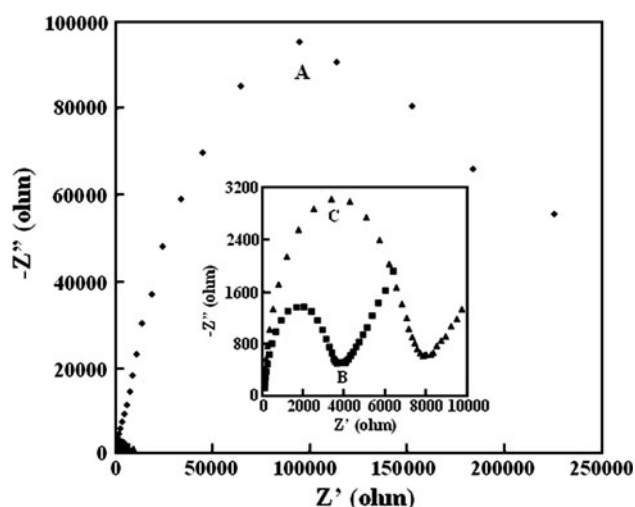


Fig. 2 Nyquist plot of Nafion/GCE (A), GCE (B) and QDs-Nafion/GCE (C) in the presence of 10 mM of $\text{Fe}(\text{CN})_6^{3-/4-}$, 0.1 M PBS (pH = 7.0): DC potential 250 mV; frequency range 0.01 Hz–100 kHz; modulation potential 10 mV

achieved with the modified electrode clearly indicate the occurrence of an electrocatalytic process on the QDs-Nafion/GCE modified electrode.

The catalytic effect of QDs on ORR at QDs-Nafion/GCE was studied over a pH range 3.8–8.0. At pHs lower than 5.4, no cathodic peak was observed for ORR because in these pHs, the CdTe QDs are not stable. At higher pH of buffer solution, a gradual increase in the cathodic peak current up was observed until a pH of 7.0–8.0 is reached. A pH of 7.0 with maximum cathodic current enhancement was then selected for electrocatalytic reduction of dioxygen. In our previous work [23], we also found that oxygen is reduced bioelectrocatalytically to water at natural pH.

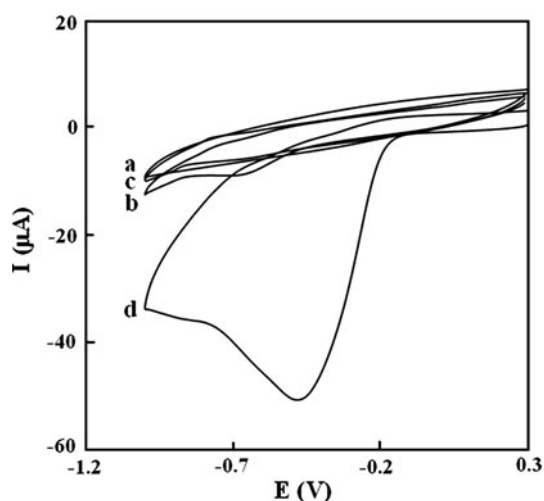


Fig. 3 Cyclic voltammograms of GCE in the absence (a) and presence (b) of oxygen and QDs-Nafion/GCE in the absence (c) and presence (d) of oxygen (pH, 7.0; scan rate, 100 mV s^{-1})

Figure 4 illustrates the cyclic voltammograms obtained in an oxygen-saturated solution of pH 7.0 on the QDs-Nafion/GCE at different scan rates. Figure 4A shows that at low scan rates (i.e., 10 mV s^{-1} and lower), the CVs are composed of two peaks, revealing the occurrence of two cathodic processes. The first one localized at -0.45 V can be associated to the electrochemical reduction process of molecular oxygen to hydrogen peroxide, which is in the peroxide form (OOH^-) in neutral pHs [24, 25].

It is noteworthy that, based on previous reports [26], Cd is a two-valent species, with two stable forms, Cd^{2+} and Cd^0 , and an unstable intermediate valence, Cd^+ . While, due to its inherent instability, Cd^+ may capture or release an electron to form a stable valence (Cd^0 or Cd^{2+}). In fact, the excess Cd^{2+} at the surface of electrode may

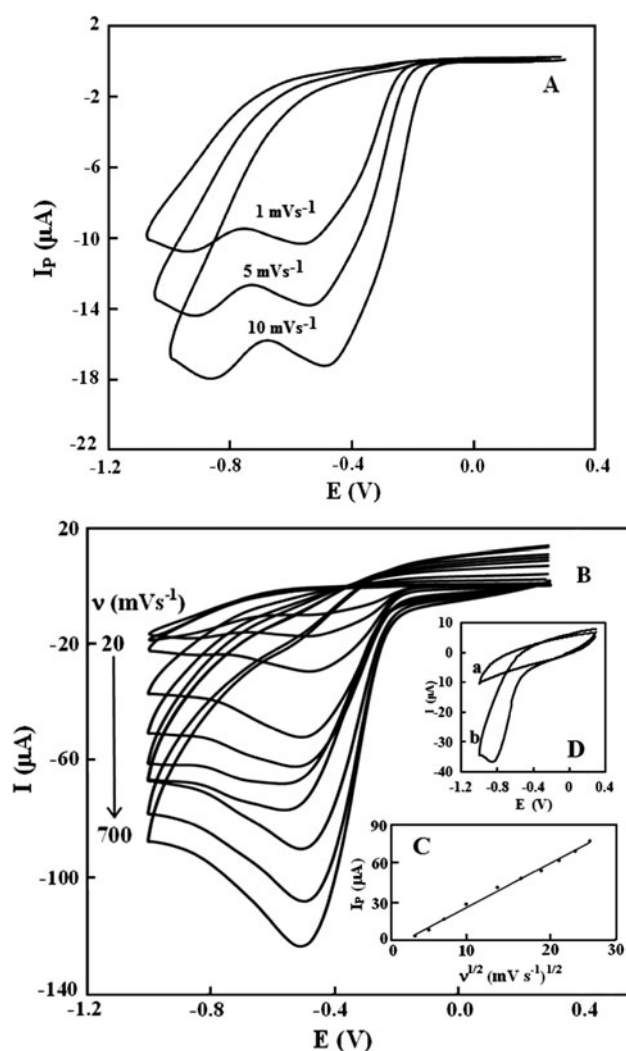
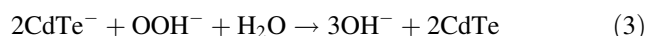
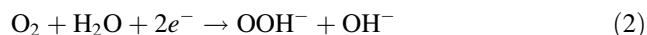


Fig. 4 Cyclic voltammograms of QDs-Nafion/GCE in obtained in oxygen-saturated 0.20 M PBS (pH 7.0) at low (A) and high scan rates (B). Plot of I_p versus $\nu^{1/2}$ (C) and cyclic voltammograms of QDs-Nafion/GCE in deaerated 0.2 M PBS (pH 7.0) in the absence (a) and presence of 2 mM H_2O_2 with scan rate of 100 mV s^{-1} (D)

capture an electron at -0.45 V to form Cd^+ in the cathodic direction, the captured electron being shared among the excess Cd^{2+} at the surface. Considering the properties of two-equivalent species and the resonance structure of Cd^+ [27], it is postulated that the resulting Cd^+ in the vacancy may inject an electron to H_2O_2 , due to its instability, and act as a catalytic intermediate in the reduction of H_2O_2 . The reduction and evaluation of H_2O_2 occurred in the potential of -0.85 V. The corresponding processes are as follows:



However, at scan rates >10 mV s^{-1} (Fig. 4B), the electron transfers in the two steps are coupled and only one peak can be observed.

As shown in the inset of Fig. 4C, a plot of I_p versus $v^{1/2}$ gives a straight line with correlation coefficient of 0.9954, suggesting that the kinetics of the overall process are controlled by mass transport of dioxygen from the bulk solution to the electrode surface, controlled by the diffusion on this electrode.

To survey the proposed mechanism, the cyclic voltammogram of QDs–Nafion/GCE was obtained in a buffer solution of pH 7.0 in the absence of O_2 (Fig. 4D, curve a). This voltammogram do not show any peaks, which confirmed that the appeared peaks in Fig. 4 are corresponding to dioxygen reduction. Then, 10 ml of 10 mM H_2O_2 was added to the deaerated buffer solution and its CV was obtained (Fig. 4D, curve b). As is obvious, the obtained cyclic voltammogram shows a sharp peak in the potential of -0.85 V versus Ag/AgCl. The results thus obtained confirm that the second peak in Fig. 3 corresponds to the reduction of H_2O_2 .

The RDE voltammograms for an O_2 saturated buffer solution of pH 7.0 at various rotation rates using the modified glassy carbon rotation disk electrode were also recorded. Typical current potential curves are shown in Fig. 5. Similar to the results obtained with cyclic voltammetry, one reduction step is recorded at this electrode. The modification of GCE with QDs resulted in an obvious positive shift of the half-wave potential and a larger current density, which is most possibly attributed to the higher surface area of QDs.

The corresponding Levich plot of limiting current “ $I_{l,c}$ ” versus $\omega^{1/2}$ [27], where “ $I_{l,c}$ ” is defined as the difference between the currents obtained at the surface of modified electrode at -0.60 V, is shown in Fig. 5A. As it is obvious from Fig 5A, the limiting currents increase with increasing rate of rotation and then level off. The thickness of the diffusion layer decreases with increasing rotation speed of

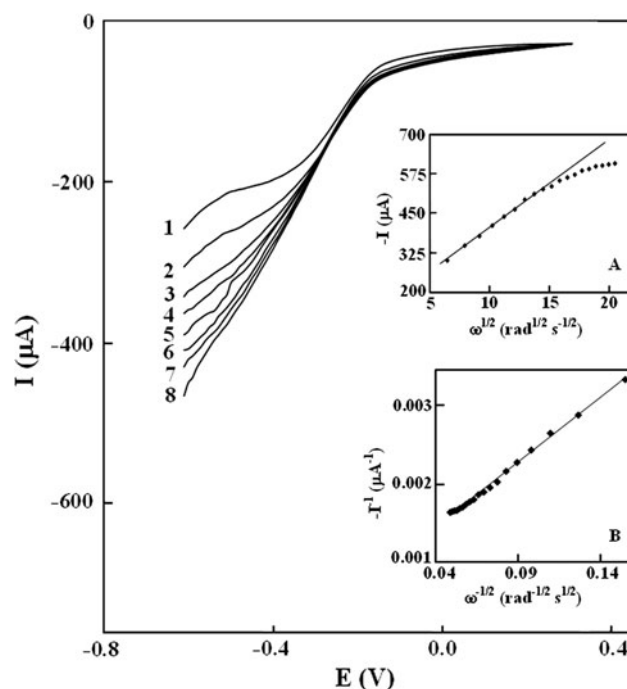


Fig. 5 RDE voltammograms of QDs–Nafion/GCE in oxygen-saturated 0.20 M PBS at various rotation rates. Scan rates are (1) 200, (2) 400, (3) 600, (4) 800, (5) 1000, (6) 1200, (7) 1400, (8) 1600. **A** Koutecky–Levich plot constructed from RDE voltammograms at -0.60 V. **B** Levich plot from Koutecky–Levich plot (scan rate: 100 mV s^{-1})

the electrode and, hence, the effect of mass transport becomes less important in overall process. Clearly the downward deviation of the limiting current with increase in rotating speed is due to the participation of the electron transition process in the limiting current. Thus, varying the rotation speed has no effect on the electron diffusion. Thus, the clear lack of linearity suggests immediately that the reaction is limited by the electrode kinetics and not by mass transport.

The relationship between the limiting current and rotation speed should obey the Levich equation:

$$I_{l,c} = 0.62nFAv^{-1/6}D_2^{2/3}\omega^{1/2}C_0 \quad (4)$$

where D , v , ω , and C_0 are diffusion coefficient, kinematic viscosity, rotation speed, and bulk concentration of the oxygen in the solution, respectively. From the slope of Levich plot, the diffusion coefficient of O_2 in the PBS could be measured as $2.08 \times 10^{-5} \text{ cm}^2 \text{ s}^{-1}$, which is comparable with the previously reported values [28, 29].

The Koutecky–Levich (K–L) plot for QDs–Nafion/GCE at -0.60 V is shown in Fig. 5B. The total number (n) of electrons transferred for the ORR can be estimated from the Koutecky–Levich equation:

$$\frac{1}{i} = \frac{1}{i_k} + \frac{1}{i_{l,c}} = \frac{1}{i_k} + \frac{1}{0.62nFAC_0D_0^{2/3}\omega^{1/2}} \quad (5)$$

where “ i ” is the measured current density, “ i_k ” is the current density in the absence of any mass-transfer effects, ω is the angular velocity of rotation, and F is the Faraday constant. The values of the concentration of O_2 (C_O) and the diffusion coefficient of O_2 (D_O) in PBS are cited as $1.2 \times 10^{-6} \text{ mol cm}^{-3}$ [28] and $2.08 \times 10^{-5} \text{ cm}^2 \text{ s}^{-1}$ from Levich equation. The value of the kinematic viscosity (ν) of PBS measured at our laboratory is $0.01 \text{ cm}^2 \text{ s}^{-1}$. Thus, we obtained a value of $n = 4.21$ (~ 4) for the ORR at the proposed modified electrode.

4 Conclusion

The surface of GCE was successfully modified using CdTe QDs and Nafion ionomers toward oxygen reduction in natural buffered medium. The prepared QDs–Nafion/GCE acts as an effective catalyst for the electroreduction of oxygen in phosphate buffer solution pH 7. Voltammetric studies indicated that reduction of oxygen at modified electrode surface is a four electron process. The oxygen diffusion coefficient was measured using Levich equation.

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